Vacuum ultraviolet $5d^14f^9$-$4f^{10}$ emission of Ho^{3+} ions in alkaline-earth fluorides

E A Radzhabov[1,2], V. Nagirnyi[3], A I Nepomnyashchikh[1,2]

[1]Vinogradov Institute of Geochemistry, Russian Academy of Sciences, Favorskii street 1a, P.O.Box 4019, 664033 Irkutsk, Russia

[2]Irkutsk State University, Physics department, Gagarin boulevard 20, 664003 Irkutsk, Russia

[3]Institute of Physics, University of Tartu, Riia 142, 51014 Tartu, Estonia

Abstract

Time-resolved emission, excitation as well as emission decay curves of CaF_2, SrF_2, BaF_2 doped with HoF_3 were investigated. Most intensive emission bands near 168 nm, having long decay time, belong to spin-forbidden transitions from $5d^14f^9$ high spin (HS) states to ground $^5I_8$ states of Ho^{3+} ions. Weak spin allowed $5d^14f^9$(LS)-$4f^{10}$ emission band at 158 nm was observed only in CaF_2-Ho crystals. Spin allowed and spin-forbidden excitation bands were observed in all crystals near 166 and 155 nm respectively. Fast component of spin-forbidden emissions due to multiphonon relaxation to low-lying $4f^{10}$ Ho^{3+} level was observed for all crystals.

Keywords:
rare-earth ions, Ho^{3+}, vacuum ultraviolet, luminescence, time-resolved, multiphonon relaxation, alkaline-earth fluorides

1. Introduction

Spectroscopy of f-d transitions of rare-earth ions doped into crystals remains relatively less investigated field of optical spectroscopy (Makhov et al., 2001). The spectroscopic investigation of $4f^n$-$5d^14f^{n-1}$ transitions of rare-earth ions (hereafter simply 4f-5d) in the vacuum ultraviolet region could help in search of new scintillators or new ultraviolet lasers materials.

For holmium two weak emissions in the vacuum ultraviolet region of the spectrum were observed at 158 nm in YF_3 and at 167 nm in $LiYF_4$ excited at 130 nm (Peijzel et al., 2002). These emissions were attributed to Ho^{3+} spin-forbidden transitions from $4f^95d$ to the ground state (Peijzel et al., 2002). The spectrum of the $LiYF_4$:Ho^{3+} crystal under F_2 laser pumping (at 157 nm) shows several bands in the spectral range from 157.6 to 190 nm. The fluorescence peaks were assigned to the spin-allowed and the spin-forbidden transitions between the levels of the $4f^95d$ and the levels of the $4f^{10}$ electronic configuration of the Ho^{3+} ion (Sarantopoulou et al., 1999). Ho^{3+} vacuum ultraviolet emission of alkaline-earth fluorides using continuous discharge lamp excitation were shortly presented in our previous papers (Radzhabov and Prosekina, 2011; Radzhabov et al., 2012).

The main goal of this paper is the time-resolved spectroscopy of Ho^{3+} ultraviolet and vacuum ultraviolet emission in CaF_2, SrF_2, BaF_2 with concentration of HoF_3 dopants ranging from 0.01 to 0.3 molar %.

2. Experimental

Crystals were grown in vacuum in a graphite crucible by the Stockbarger method (Radzhabov et al., 2012). Graphite crucible contains three cylindrical cavities 10 mm in diameter and 80 mm long, which allows to grow three crystals of Ø10x50 mm in dimensions with different impurity concentrations at the same time. Typically samples Ø10 mm x 1mm cutted from grown roads were used for optical measurements.

Time-resolved spectra and decay curves were recorded using synchrotron radiation at the SUPERLUMI station of HASYLAB at DESY (Hamburg, Germany) as described in paper (Kirm et al., 2001). Measurements were performed in the short time window (1-5 ns), in the long time window (55-80 ns), and in the time-integrated regime.

Additionally absorption and excitation spectra were measured using grating monochromator VM4 (by LOMO) under excitation of deuterium lamp L7293-50 with MgF_2 window (by Hamamatsu) and a solar-blind photomultiplier FEU142 as light detector.

3. Results

Absorption spectra of Ho^{3+} ion in all three crystals show several bands below 160 nm (Fig.1). All bands are shifted to less wavelength by few nm in a row of CaF_2 to BaF_2. Shift of absorption 4f-5d and emission 5d-4f bands in a row of CaF_2 to BaF_2 are known for other rare-earth ions, it is due to decrease of crystal field splitting of 5d levels (Radzhabov and Nepomnyashchikh, 2008).

Two 5d-4f emission bands at 167-169 and 180-183 nm were observed with intensity ratio of near 10:1 (Fig.2-4). The bands were assigned to the transitions from 5d lowest energy level to $^5I_8$ and $^5I_7$ levels of 4f shell. Four main excitation bands 155, 146, 138 and 130 nm correlate with four absorption bands (compare Figs.1 - 4). Both emission bands contain slow and fast decay components. The decay time of fast component increased

Email address: eradzh@igc.irk.ru (E A Radzhabov[1,2])

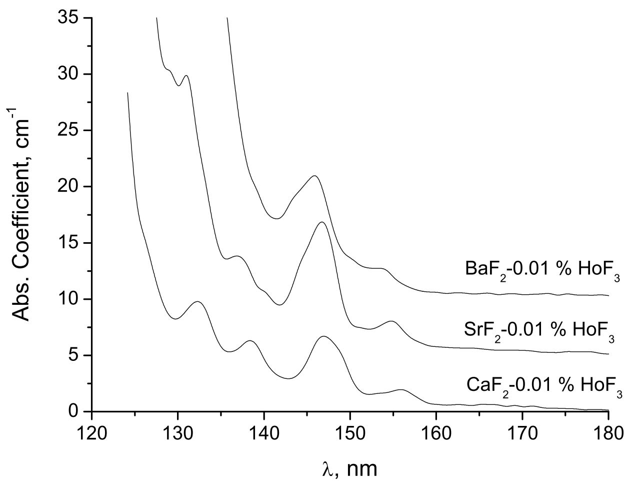

Figure 1: Absorption spectra of Ho^{3+} 5d-4f transitions in CaF_2, SrF_2, BaF_2 crystals doped with 0.01 molar % of HoF_3 at 295K. Spectra were separated by 5 cm^{-1} for better viewing.

by an order of magnitude in a row of CaF_2 to BaF_2 (Fig.5). The decay times of fast components under illumination into lowest energy excitation band near 155 nm were equal to 50, 15.7 and 4.2 ns in BaF_2, SrF_2, and CaF_2 respectively (Fig.5). The decay times become few ns longer under excitation into the 146 nm band.

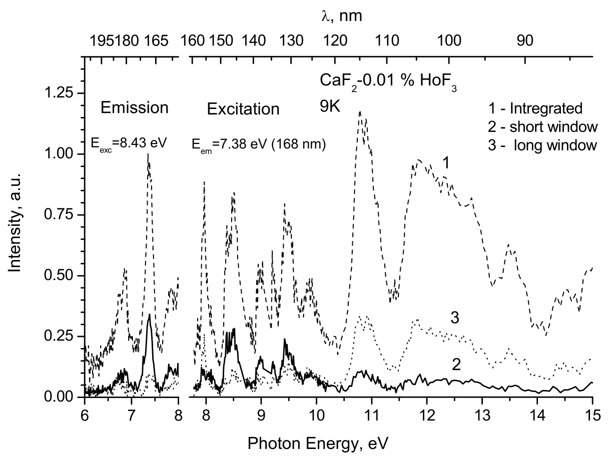

Figure 2: Emission and excitation spectra of Ho^{3+} 5d-4f transitions in CaF_2 crystals doped with 0.01 molar % of HoF_3 at 9K.

The 5d-4f emission bands are relatively weak in CaF_2 while they become more intensive in SrF_2 and BaF_2. Apart to this 4f-4f emission bands drastically decreased from CaF_2 to SrF_2, BaF_2. Two 5d-4f Ho^{3+} bands in BaF_2, SrF_2 evidently belong to transition to $^5I_8$ ground state and to $^5I_7$ first excited state of $4f^{10}$ configuration. Emission spectrum in CaF_2 is a combination of 5d(LS)-4f and 5d(HS)-4f bands.

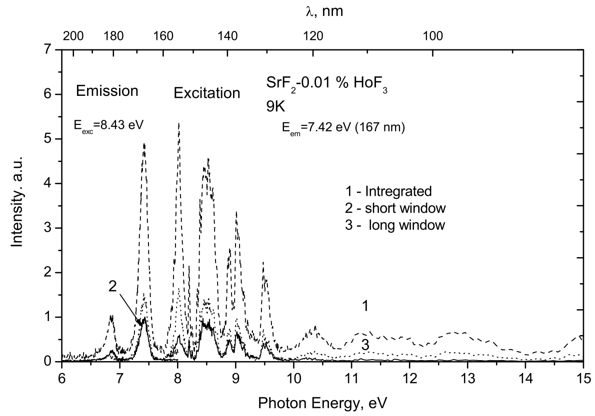

Figure 3: Emission and excitation spectra of Ho^{3+} 5d-4f transitions in SrF_2 crystals doped with 0.01 molar % of HoF_3 at 9K.

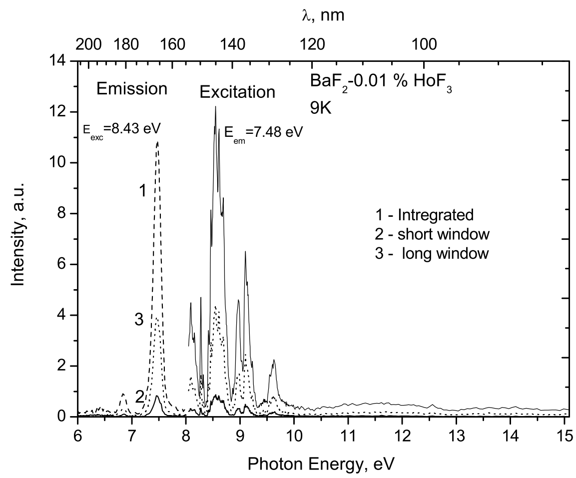

Figure 4: Emission and excitation spectra of Ho^{3+} 5d-4f transitions in BaF_2 crystals doped with 0.01 molar % of HoF_3 at 9K.

4. Discussion

The zero-phonon Ho^{3+} 4f-5d absorption and excitation lines were observed in CaF_2 at 157.1 nm (Szszurek and Schlesinger, 1985) and 157.5 nm (Pieterson et al., 2002) respectively. No spin-forbidden transitions were observed in excitation spectrum, possibly due to the low Ho^{3+} concentration (Pieterson et al., 2002). To find the spin-forbidden bands we have measured excitation spectra for integrated emission of all f-f bands within 220-800 nm wavelength range of all three hosts with concentration of HoF_3 from 0.01 to 0.3 molar % (Fig 6). Spectra were measured at room temperature because f-f emission under f-d excitation substantially decreased with decreasing temperature. New weak excitation bands were found in all hosts at long wavelength side of first 4f-4f5d bands with separation near 9 nm (see Fig.6). Bands were questionable in samples with 0.01 % of Ho, but were evident in samples con-

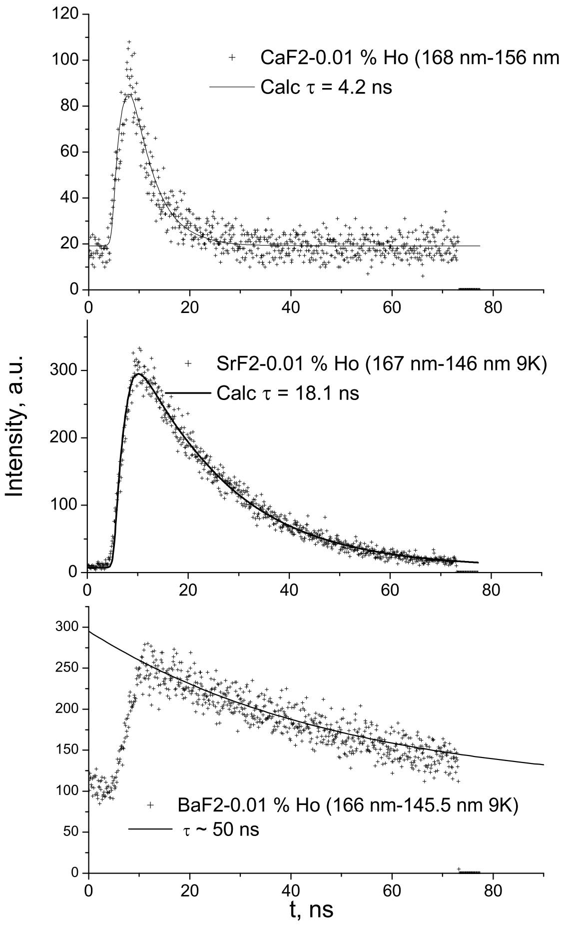

Figure 5: Decay of Ho^{3+} emission bands near 167nm in BaF_2, SrF_2, CaF_2 crystals doped with 0.01 molar % of HoF_3 at 9K.

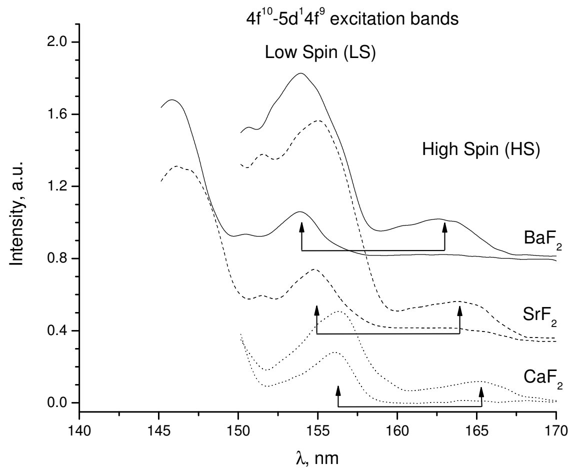

Figure 6: Excitation spectra of Ho^{3+} 5d-4f transitions in CaF_2, SrF_2, BaF_2 crystals doped with 0.01 molar % of HoF_3 (lower curves) and by 0.03 molar % of HoF_3 at 295K. Spectra were separated for best viewing. Splitting of first excitation bands by transitions to low spin and high spin 5d4f9 states shown by arrows.

taining 0.3 % of HoF_3 (see Fig 6). These excitation bands are attributed to transitions to high-spin 5d4f states. Energy gaps between Ho^{3+} 4f5d(HS) and 4f5d(LS) states is near 3500 cm^{-1} for all CaF_2, SrF_2, BaF_2 hosts, which is close to that observed in $LiYF_4$-Ho (3460cm^{-1}) (Pieterson et al., 2001). We conclude that the emission band near 158 nm in CaF_2 -Ho belongs to spin-allowed transitions from 5d4f(HS) and the most intensive emission band near 169 nm belongs to spin-forbidden transitions from 5d4f(LS) to ground state. Energy splitting between 4f5d(HS) and 4f5d(LS) emission and excitation bands in CaF_2 -Ho is the same (compare Fig.2 and Fig.6). No spin-allowed transitions were observed in SrF_2 -Ho or BaF_2 -Ho crystals (see also (Radzhabov et al., 2012)). The absence of spin-allowed emission bands in SrF_2 and BaF_2 is not yet clear.

It is known that nonradiative transfer probability from some f level to underlying levels exponentially decrease with energy gap between levels (so called energy gap law) (Henderson and Imbush, 1989; Sole et al., 2005). Reformulation of this law in term of number of effective phonons allows to conclude that nonradiative processes are dominant for processes involving less than 4-6 effective phonons (Henderson and Imbush, 1989). Comparison of ultraviolet Nd emission in a number orthoborate and orthophosphate crystals lead to the conclusion that nonradiative transition from 5d level to lower lying 4f level is predominant when energy gap is less than the energy of 5 phonons (Wegh et al., 2001).

The frequencies of a longitudinal optic phonon obtained from optical data at 5 K are 484, 397 and 346 cm^{-1} for CaF_2, SrF_2, BaF_2 respectively (Hayes, 1974). The highest observed Ho^{3+} $4f^{10}$ level is $^3K_7$, transitions to this level were observed at 170.5 nm in $LiYF_4$ (Peijzel et al., 2002). $4f^95d^1$ (HS) excitation bands were measured at 162.5, 164, 165 nm in CaF_2, SrF_2, BaF_2, respectively (see Fig.6). Therefore the energy gap between these two levels are near 2000, 2300, 2900 cm^{-1} or around 4, 6, 8 phonon frequencies in CaF_2, SrF_2, BaF_2, respectively. It follows that nonradiative multiphonon energy transfer of Ho^{3+} from $5d4f^9$(HS) to $4f^{10}$ ($^3K_7$) level should be most effective in CaF_2 and much less effective in BaF_2. As the result, the $5d4f^9$-$4f^{10}$ band intensity is increased and $4f^{10}$-$4f^{10}$ bands intensities sharply decreased in a row of CaF_2 to BaF_2. The fast decay components of spin-forbidden bands obviously should be assigned to multiphonon transition from 5d to $4f^{10}$. According to increase the energy gap the fast decay time become drastically longer in a row of CaF_2, SrF_2, BaF_2 (see Fig.5). The nonradiative relaxation rate decreased with decreasing temperature, as number of phonons becomes lesser (Henderson and Imbush, 1989). According to this the Ho^{3+} f-f line intensities are several times decreased from 78K to 6.7K under f-d excitation (Radzhabov et al., 2012). The host and temperature variations of 5d-4f and 4f-4f intensity and decay times after 4f-5d excitation could be described in term of nonradiative multiphonon energy transfer from high spin lowest 5d level to the low-lying $4f^{10}$($^3K_7$) level.

The dependence of the multiphonon relaxation probability on

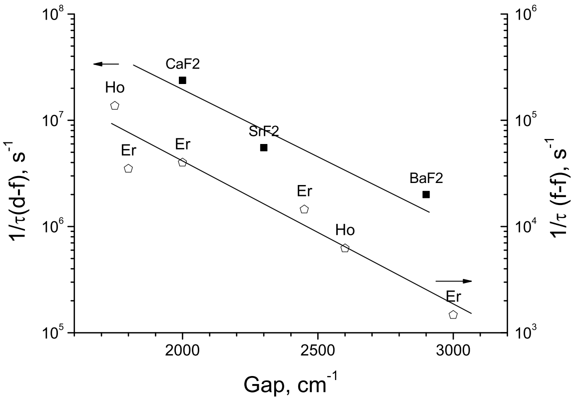

Figure 7: Energy-gap dependence of the multiphonon transition rate for f-f transition in SrF_2-RE taken from Riseberg and Moos, 1968 and for d-f transition of Ho^{3+} in alkaline-earth fluorides

the energy gap, disregarding any selection rules, is of the form (van Dijk and Schuurmans, 1983)

$$k_{NR} = \beta e^{-\alpha \Delta E}$$

where β and α are constants which are characteristic of the particular crystal and ΔE is the electronic energy "gap" between the 4f levels. However, the β varies by a factor of 10^5. This wide variation is due to a considerable dependence of β on the vibrational coupling to the host lattice (van Dijk and Schuurmans, 1983). While there are number of papers on measurements of multiphonon f-f relaxation, but to our knowledge, no such measurements on d-f relaxation have been made.

We plot the inverse decay times of fast components of spin-forbidden $5d^1 4f^9$-$^5I_8$ bands near 168 nm versus the energy gap between 5d and nearest 4f levels (Fig.7). Three hosts CaF_2, SrF_2, BaF_2 have the same crystal structure and slightly differ with anion-cation distances. Therefore, in the first approximation, the data for d-f multiphonon relaxation in three alkaline earth fluorides could be compared with that of f-f relaxation in SrF_2, which we took from paper (Riseberg and Moos, 1968). Note that the slope α for both dependencies is nearly the same while the constant β is thee order higher for d-f multiphonon relaxation (see Fig.7). The constant β reflects the interaction of orbitals with phonons. Therefore it is not surprising that constant β is much larger for d-f relaxation than for f-f multiphonon relaxation, because the d-orbital has much greater intersection with orbital of surrounding host ions.

5. Conclusion

Ho^{3+} $5d^1 4f^9$-$4f^{10}$ emission in vacuum ultraviolet were found in CaF_2, SrF_2, BaF_2 crystals. Two bands are observed : strongest ones at 166-168 nm and weaker bands at 182-184 nm. The bands are associated with spin forbidden transition from $5d^1 4f^9$ to $^5I_8$, $^5I_7$ respectively. Weaker spin-allowed $5d^1 4f^9$-$^5I_8$ band at 158 nm is observed in CaF_2 only. Decrease of total intensity of f-f bands in compare with that of d-f bands as well as increase fast decay times of spin-forbidden emission in a row of CaF_2-BaF_2 caused by increasing number of phonons in the process of nonradiative multiphonon energy transfer from lowest 5d level to nearest $4f^{10}$ excited level.

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